Crystal structure of 4-methoxycarbonyl-1,3-dithiole-2-thione, C5H4O2S3

Crystal structure of 4-methoxycarbonyl-1,3-dithiole-2-thione, $C_5H_4O_2S_3$

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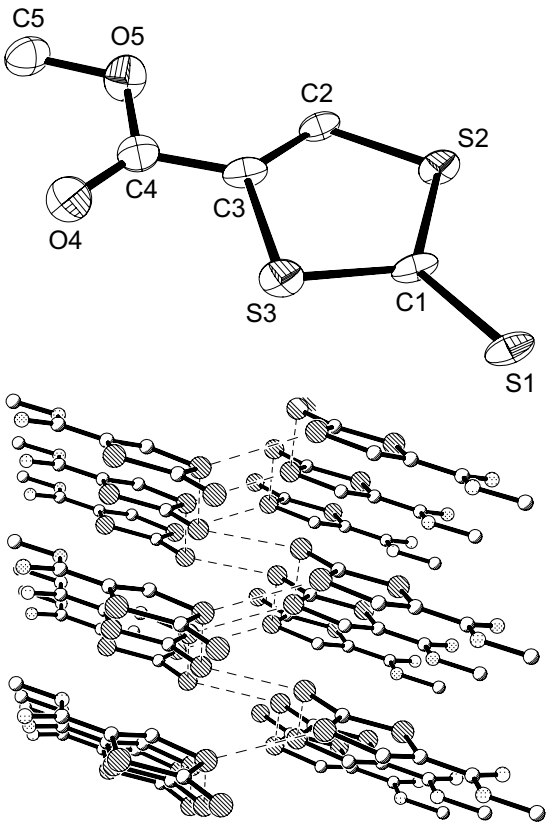
Received November 6, 2006, accepted and available on-line March 23, 2007; CCDC no. 1267/1927



Abstract

$C_5H_4O_2S_3$, monoclinic, $P12_1/c1$ (no. 14), a = 3.9797(1) Å, b = 6.0394(2) Å, c = 31.1165(6) Å, β = 91.868(1)°, V = 747.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.119, $wR_{ref}(F^2)$ = 0.324, T = 200 K.

Source of material

In the literature 4-methoxycarbonyl-1,3-dithiole-2-thione was obtained in three steps [1]. In the present one-pot synthesis the title compound was obtained under solvent free conditions catalyzed by potassium cyanide in the presence of silica as solid support at 200 °C (85 % yield). 0.2 mmol of 4,5-bis(carbonylmethoxy)-1,3-dithiole-2-thione, 0.4 mmol of potassium cyanide and 0.2 g of silica were mixed in a mortar. This powder was heated for 1 h at 200 °C. The color of the mixture was turned from yellow to light brown. The pure compound was obtained by filtration of the solution in dichloromethane, followed by evaporation of solvent and preparative chromatography over silica gel. The product was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

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Experimental details

The X-ray reflections were rather broad and diffuse, but the data turned out to be useable. All hydrogen atoms were treated using appropriate riding models. The bad quality of the crystals and the dataset were the reasons for the large R values.

Discussion

Ever since the discovery of the first metallic charge transfer complex composed of TTF (tetrathiafulvalene) and TCNQ (tetracyanoquinodimethane) [2], modifications of the TTF skeleton have received considerable attention from synthetic chemists in exploration of new molecular-based organic metals. Phosphite cross-couplings for the preparation of functionalized TTF derivatives were first investigated because this method is generally simple when yields are good and when products are separable [3-6]. Thus the interest in the synthesis of various 1,3-dithiole-2-chalcogenone is evident, and promoted us to take up this project.

As expected the interatomic distances determined in the 1,3-dithiole-2-thione unit are all similar to analogous values known from the literature. The heterocyclic five-membered dithiolethione ring is planar, and also the carboxyl group stands in the same plane, thus is completely in conjugation. The crystal packing is dominated by very short sulfur···sulfur contacts involving two of the three sulfur atoms and building two-dimensional double layers of molecules. The S1···S1 contacts with 3.51 Å, the S1···S2 contacts with 3.55 Å, and the S2···S2 contacts with 3.42 Å are much shorter than the sum of the van der Waals radii of 3.7 Å [8].

Table 1. Data collection and handling.

Crystal:	yellow polyhedron, size 0.05 × 0.24 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.21 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6320, 1419
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1266
$N(param)_{refined}$:	92
Program:	SHELXTL [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.6598	0.8751	0.4062	0.026
H(5A)	4*e*	1.1270	0.8647	0.2795	0.054
H(5B)	4*e*	0.9949	1.1074	0.2908	0.054
H(5C)	4*e*	0.7506	0.9358	0.2661	0.054

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.0990(8)	0.1705(5)	0.4564(1)	0.029(2)	0.012(1)	0.044(2)	–0.008(1)	0.005(1)	0.001(1)
S(2)	4*e*	0.3996(7)	0.6179(4)	0.45127(9)	0.031(2)	0.007(1)	0.034(2)	–0.004(1)	0.004(1)	–0.002(1)
S(3)	4*e*	0.3851(8)	0.3412(5)	0.3752(1)	0.033(2)	0.009(1)	0.035(2)	–0.001(1)	0.002(1)	–0.004(1)
C(1)	4*e*	0.282(3)	0.364(2)	0.4288(4)	0.019(5)	0.004(5)	0.041(6)	–0.002(4)	0.001(5)	0.003(4)
C(2)	4*e*	0.569(3)	0.730(2)	0.4060(4)	0.020(6)	0.011(5)	0.035(6)	–0.004(4)	0.002(4)	0.002(4)
C(3)	4*e*	0.567(3)	0.605(2)	0.3703(4)	0.019(5)	0.006(5)	0.038(6)	0.001(4)	–0.001(4)	0.001(4)
C(4)	4*e*	0.687(3)	0.661(2)	0.3282(4)	0.020(6)	0.026(6)	0.033(6)	0.004(5)	–0.001(5)	0.001(5)
O(4)	4*e*	0.675(2)	0.547(2)	0.2971(3)	0.037(5)	0.028(5)	0.039(5)	0.002(4)	0.004(4)	–0.004(4)
O(5)	4*e*	0.818(2)	0.871(2)	0.3284(3)	0.045(5)	0.021(5)	0.038(5)	0.001(4)	0.005(4)	0.003(4)
C(5)	4*e*	0.932(3)	0.951(2)	0.2880(4)	0.035(7)	0.031(7)	0.042(8)	–0.007(6)	0.002(6)	0.009(6)

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